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(54) PRODUCTION OF CARBOXYLIC ACIDS OR DICARBOXYLIC ANHYDRIDES

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of carboxylic acids or dicarboxylic anhydrides by catalytic oxidation of hydrocarbons.

The oxidation of hydrocarbons into carboxylic acids or dicarboxylic anhydrides is a technical problem which has had widespread attention. It has acquired industrial importance particularly for the production of maleic anhydride from benzene and of phthalic anhydride from naphthalene or o-xylene. In carrying this reaction out in practice use is mainly made of catalytic air oxidation, i.e. atmospheric nitrogen is used as an inert carrier gas. Having regard to the cheapness of this gas it is not surprising that this method has hitherto been regarded as the optimum solution in the oxidation of hydrocarbons although this method is confined by the explosion limit of for example 44 g of naphthalene or o-xylene per cubic meter (STP) of air.

We have now found that the continuous production of carboxylic acids and/or dicarboxylic anhydrides by catalytic oxidation of hydrocarbons in which the hydrocarbon is passed over the catalyst by means of an inert carrier gas containing oxygen can be carried out considerably more advantageously by using as the carrier gas the carbon dioxide formed in the oxidation which is recycled for this purpose and is nitrogen-free.

The new process is suitable for the production of carboxylic acids or dicarboxylic anhydrides from the corresponding hydrocarbons, particularly of maleic acid or maleic anhydride from benzene or C₆ hydrocarbons, of acrylic acid from propylene and of phthalic anhydride from naphthalene or

o-xylene. The production of phthalic anhydride from o-xylene is of particular industrial significance.

The catalytic oxidation may be carried but for example in conventional tubular reactors in contact with fixed bed catalysts containing vanadium pentoxide at temperatures of from 350° to 500°C. For example the tubular reactor provided with a salt bath heat exchanger described in German Laid-Open Specification (DOS) No. 1,643,703 may be used which is charged with a globular supported catalyst consisting of an inert nonporous carrier to which is applied a catalytic material containing from 1 to 40% and advantageously from 1 to 25% by weight of vanadium pentoxide and from 60 to 99% and advantageously from 75 to 99% by weight of titanium dioxide. It is also possible to use other fixed bed catalysts conventionally used for the oxidation of naphthalene or o-xylene such as are described for example in German Laid-Open Specifications (DOS) Nos. 1,442,590, 1,769,998, 2,106,796 and 2,159,441.

The essential difference of this invention from the said prior art methods and, for example, the method of U.K. Specification 461,949 is that the carrier gas used for passing the hydrocarbon and oxygen into the reactor is not atmospheric nitrogen but a carrier gas containing carbon dioxide formed in the oxidation. For example the mixture of oxygen and carrier gas may contain from 72 to 95% and preferably from 80 to 90% by volume of carbon dioxide, from 0.1 to 3% by volume of carbon monoxide and from 5 to 25% and preferably from 12 to 18% by volume of oxygen. The use of the said gas mixture has the advantage that any concentration of naphthalene and o-xylene may be used without any risk of explosion. For example loadings of from 45 to 300 g and preferably from 160 to 220 g of naphthalene or o-xylene per cubic meter (STP) of mixtures of oxygen and carrier gas are possible.

The carrier gas may be introduced into

the apparatus together with the oxygen at the beginning of the reaction. This is recommended when full efficiency of the plant is required from the start. It is also possible at the start however to use ambient air as carrier gas for the hydrocarbon, the conventional prior art low concentration of hydrocarbon being maintained at first. In this case in the course of recycling both the desired composition of the carrier gas and the higher loading of hydrocarbon may be set up after a short time. It is not necessary to supply carbon dioxide. In continuous operation the desired composition of the gas may easily be maintained by continuous replacement of the oxygen which has been used up and release of the excess gas to the atmosphere.

Setting up the oxygen content of the recycle gas does not offer any difficulty and can be effected with adequate reliability with conventional measuring apparatus. Since when using o-xylene explosion cannot occur with any xylene content when the oxygen content is less than 19% by volume and similarly no ignition can occur at a loading of more than 95 g per cubic meter (STP) at a content of 19% by volume of oxygen, operation within a safe working range is ensured. Care has to be taken of course to ensure that the o-xylene is uniformly dispersed in the gas stream because the o-xylene content in the process according to the invention is from about 1 to 5% and preferably from 2 to 4.5% by volume. The mixture of carrier gas, oxygen and hydrocarbon may be introduced into the reactor in the conventional manner, for example through a blower, at a temperature of from 80° to 250°C. Oxidation takes place for example at a temperature of from 370° to 420°C. The oxidation is advantageously carried out at a pressure of from 0.8 to 5 and preferably at from 1 to 3 atmospheres gauge. After the gas from the process has left the reactor it is cooled to 210°C to 170°C for example by means of gas coolers, and fed to appropriate separating means for separation of the carboxylic acid or the anhydride formed. Because of the high concentration of product in the process gas made possible by the process, for example the main portion of the phthalic anhydride formed in the production of phthalic anhydride may be separated in liquid form in contact with cooled surfaces. The process gas is therefore preferably first passed through a liquid separator and only then flows through one or more, preferably two, desublimators, for example finned tube separators, for the separation of phthalic anhydride.

The stream of gas which leaves the separator at about 50° to 60°C is scrubbed. For this purpose the stream of gas may be

treated for example with water or preferably with from 15 to 35% aqueous solution of maleic acid, conveniently at a temperature of from 35° to 55°C, the wash liquid advantageously being circulated. The content of organic acids in the recycle gas may be kept at less than 30 mg per cubic meter (STP) by this method.

The recycle gas purified in this way is then fed to the reactor for fresh loading with hydrocarbon and oxygen. An advantageous procedure is to remove the excess offgas from the recycle gas leaving the gas scrubbing and then to heat the remainder to 60° to 150°C and preferably to 80° to 120°C. The amount of offgas removed from the recycle gas after the gas scrubbing may be for example 3.6% by volume of the circulating stream of gas for example at a throughput of 120 g of o-xylene per cubic meter (STP).

The new process makes possible a particularly advantageous production of carboxylic acids and dicarboxylic anhydrides. For example since it is not necessary (in contrast to conventional methods) to maintain explosion limits in the production of phthalic anhydride from o-xylene or naphthalene, the hydrocarbons may be used in high concentrations. The carbon dioxide carrier gas surprisingly also has the advantage that the oxygen content of the recycle gas is utilized much better than is possible when using air. The carbon dioxide on the one hand moderates the reaction to a very marked extent, evidently by improved withdrawal of heat, so that no pronounced peak temperatures are obtained. On the other hand it is apparently able to act itself as an oxidizing agent at the prevailing temperatures, at least with respect to the catalyst. Thus it is apparent that the high oxygen concentration with in the prior art methods has been thought to be necessary to maintain the oxidation condition of the catalyst can be dispensed with in the new process. Whereas for example in the prior art method only about 2 to 3% of the oxygen content of the air is used and more than 97% of the gas which has been conveyed with considerable expenditure of energy is returned to the atmosphere laden with heat and pollutants, about 12% of the circulating gas is utilized for the reaction in the process of the invention and only about 5% of the gas has to be returned to the atmosphere as excess gas. The said offgas contains only a small amount of carbon monoxide as in the prior art method because the content of carbon monoxide in the recycle gas surprisingly has not been found to increase.

In the production of phthalic anhydride from o-xylene using the catalyst described in German Laid-Open Specification (DOS) 130

No. 1,442,590 the reaction along the reaction tube proceeds somewhat differently from the prior art course. The carbon dioxide has an appreciable effect on the reaction by the high energy absorption of the molecule per se and as end product. On the one hand overheating of the active reaction layer is damped by the increased conveyance of energy and on the other hand the withdrawal of sensible heat of reaction is accelerated by better heat transfer through the wall of the tube. The result of this is that the reaction zone is longer and no pronounced hot spot zone is formed. The milder reaction conditions result in a considerable increase in the yield. In the method of the invention an increase in yield is obtained which may amount to up to 15% under favorable conditions. This increase in yield in combination with the other advantages more than compensates for the supply of pure molecular oxygen. Moreover there is a considerable decrease in the separation surface area. Thus hitherto an area of about 130 square meters has been necessary in the form of expensive finned tubes for 1000 cubic meters of reaction gas. In contrast in the Example according to the invention a finned tube separation surface of about 7 square meters is necessary for 300 cubic meters (STP) per hour.

The following Example illustrates the invention.

EXAMPLE

200 g of o-xylene is injected at 160°C into each cubic meter (STP) of a recycled carrier gas stream consisting of 81.5% by volume of carbon dioxide, 0.5% by volume of carbon monoxide and 18% by volume of oxygen. The carrier gas loaded with o-xylene is passed through a heated cyclone to evaporate any entrained droplets. The gas mixture flows into a reactor which consists of twenty parallel tubes having an internal diameter of 32 mm which are filled for a length of 3 meters with the catalyst described in German Laid-Open Specification (DOS) 1,442,590. The pressure upstream of the reactor is kept at 2.2 atmospheres gauge. 300 cubic meters (STP) of gas is passed through per hour. Oxidation takes place in the reactor at temperatures of from 400° to 500°C. The oxygen content in the gas stream falls to less than 5% by volume while the content of carbon monoxide in the circulating gas remains constant. The pressure falls to 0.8 atmosphere gauge. In cooler downstream of the reactor and in which steam is produced at 2 atmospheres gauge the gas is cooled to 135°C. Most of the phthalic anhydride formed is separated in liquid form and flows down into a collecting trough. The gas which remains is

supplied to two interchangeable separators or desublimators in which phthalic anhydride is separated down to a residual content of 100 mg per cubic meter (STP). The two separators are alternately melted off with steam at 20 atmospheres gauge. This alternation takes place hourly. 7 square meters of separator surface in the form of finished tubes is necessary for the separation. 72 kg of phthalic anhydride (equivalent to 88.5% of theory) is obtained per hour in the phthalic anhydride collecting trough. Byproducts of the oxidation (maleic anhydride and benzoic acid) pass together with the gas mixture to the separator system and pass at a temperature of 50°C into a scrubbing system. The scrubbing liquid is a recycled 30% aqueous solution of maleic acid. After the recycle gas has left the scrubbing system and contains less than 50 mg of organic acids per cubic meter under the pressure of the system, 18 cubic meters (STP) is removed per hour as offgas. The recycle gas is then reheated to 115°C immediately with 2 atmospheres gauge steam and fed into the recycle gas blower where the heat of compression causes heating up of the gas stream to 150°C. The recycle gas stream thus remains always in a completely dry condition far above the dew-point of water vapor which is present. The gas leaving the blower is replenished with oxygen to the necessary content and after having been loaded with o-xylene is again supplied to the oxidation.

WHAT WE CLAIM IS:—

1. A process for the continuous production of a carboxylic acid and/or a dicarboxylic anhydride by catalytic oxidation of a hydrocarbon in which the hydrocarbon is passed over the catalyst by means of an inert carrier gas containing oxygen, wherein the carrier gas is carbon dioxide formed in the oxidation which is recycled for this purpose and is nitrogen-free.
2. A process as claimed in claim 1 wherein the mixture of oxygen and carrier gas contains from 72 to 95% by volume of carbon dioxide, from 0.1 to 3% by volume of carbon monoxide and from 5 to 25% by volume of oxygen.
3. A process as claimed in claim 1 or 2 wherein phthalic anhydride is prepared from o-xylene.
4. A process as claimed in claim 3 wherein the mixture of oxygen and carrier gas is loaded with from 45 to 300 g. of o-xylene per cubic meter (STP).
5. A process as claimed in claim 4 wherein the mixture of oxygen and carrier gas is loaded with from 160 to 220 g of o-xylene per cubic meter (STP).

6. A process as claimed in claim 1
carried out substantially as described in the
foregoing Example.

7. A carboxylic acid or dicarboxylic
5 anhydride when obtained by a process as
claimed in any of claims 1 to 6.

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